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4중 가교 산소 리간드를 함유한 1차원 아연 배위 고분자: $[Zn_4(1,3\text{-}BDC)_3(\mu_4\text{-}O)(pyridine)_2]$ (1,3-BDC=1, 3-benzenedicarboxylate)

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1-Dimensional Zinc Polymer Containing the Quadruply Bridging Oxygen Ligand: $[Zn_4(1,3\text{-}BDC)_3(\mu_4\text{-}O)(pyridine)_2]$

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요 약

피리딘 존재 하에서 zinc(II) nitrate ($Zn(NO_3)_2 \cdot 6H_2O$)와 1,3-$BDCH_2$ (1,3-BDC=1,3-benzenedicarboxylate)의 수열 · 용매 반응으로 1차원 배위 고분자 [Zn(1,3-BDC)(μ_4-O)(pyridine)$_2$] (**1**)이 얻어졌다. X-ray 구조 결정 결과, 고분자 **1**이 4중 가교 산소 리간드를 갖고 있음이 밝혀졌다. 고분자 **1**는 2개의 띠로 구성되어 있으며, 각 띠는 1,3-BDC 리간드에 의해서 단위체들이 연결되어 된다.

Abstract

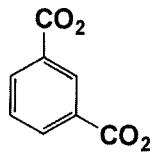
The hydro(solvo)thermal reaction of zinc(II) nitrate ($Zn(NO_3)_2 \cdot 6H_2O$) with 1,3-$BDCH_2$ (1,3-BDC=1,3-benzenedicarboxylate) in the presence of pyridine a gave 1-dimensional zinc polymer [Zn(1,3-BDC)(μ_4-O)(pyridine)$_2$] (**1**). X-ray structure determination revealed that polymer **1** has a quadruply bridging oxygen (μ_4-O) ligand. This polymer consists of two strands linked by 1,3-BDC ligands, and each strand is formed by connecting the monomer units by 1,3-DBC ligands.

1. Introduction

Recently, a variety of coordination polymers based on metal-ligand coordinative covalent bonding have received considerable attractions due to their novel topology and interesting functions.[1-6] In particular, much attention has been paid to porous high-dimensional coordination polymers, because of their potential zeolite-like applications.[7-10]

In the preparation of multi-dimensional coordination polymers, appropriate ligands play a fundamental role in determining the structural outcome of target polymers. We recently prepared several coordination polymers based on a mixed-ligand system possessing dicarboxylates and bipyridyls by hydrothermal or hydro(solvo)thermal reactions.[11-23] As a continuation of our work, we set out to prepare zinc coordination polymers based only on the dicarboxylate, 1,3-benzenedicaboxylate (1,3-BDC, a coordination angle=120°), in the presence of pyridine with an attempt to introduce it into the resulting polymer as a guest molecule.

On the contrary to out initial hope, the hydro (solvo)thermal treatments of zinc(II) nitrate ($Zn(NO_3)_2 \cdot 6H_2O$) with 1,3-$BDCH_2$ in the presence of pyridine a gave 1-dimensional zinc network. In this contribution, we report a 1-D zinc coordination polymer, Zn(1,3-BDC)(μ_4-O)(pyridine)$_2$ (**1**), which has a quadruply bridging oxygen (μ_4-O) ligand.



1,3-BDC

pyridine

2. Experimental Section

Zinc(II) nitrate, 1,3-BDCH$_2$, and pyridine (C_6H_5N) were purchased from Aldrich company. IR spectra were recorded with a Nicolet 320 FTIR spectrophotometer. Elemental analyses were performed with EA1110 (CE instrument, Italy) at the Korea Basic Science Institute.

Table 1. X-ray data collection and structure refinement for 1

empirical formula	$C_{34}H_{22}N_2O_{13}Zn_4$
fw	928.02
temperature, K	293(2)
crystal system	monoclinic
space group	$P2_1/n$
a, Å	10.344(3)
b, Å	18.030(3)
c, Å	18.033(3)
β, deg	90.46(2)
V, Å^3	3363(1)
Z	4
d_{cal}, g cm^{-3}	1.833
μ, mm^{-1}	2.891
F(000)	1856
T_{min}	0.3368
T_{max}	0.7618
2θ range (°)	3.5-50
scan type	ω
scan speed	variable
No. of reflns measured	6236
No. of reflns unique	5889
No. of reflns with $I>2\sigma(I)$	4977
No. of params refined	478
Max., in Δρ (e Å^{-3})	0.514
Min., in Δρ (e Å^{-3})	-0.769
GOF on F^2	1.033
R	0.0349
wR_2[a]	0.0850

[a] $wR_2=\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$

Table 2. Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2×10^4)

	x	y	z	U(eq)
Zn(1)	6595(1)	3295(1)	1743(1)	35(1)
Zn(2)	3654(1)	3242(1)	1720(1)	34(1)
Zn(3)	5118(1)	3173(1)	3223(1)	43(1)
Zn(4)	5192(1)	1779(1)	1833(1)	43(1)
O(1)	6722(2)	1454(2)	1285(2)	45(1)
O(2)	7875(2)	2466(2)	1521(2)	55(1)
O(3)	13574(2)	1418(2)	1391(2)	49(1)
O(4)	12482(2)	2483(1)	1325(2)	45(1)
O(5)	3424(2)	6219(1)	-770(1)	41(1)
O(6)	4882(3)	7111(2)	-613(2)	56(1)
O(7)	3571(2)	4206(1)	1209(1)	41(1)
O(8)	5020(3)	4387(2)	2103(2)	60(1)
O(9)	6661(2)	3753(2)	3513(1)	45(1)
O(10)	7796(2)	3721(2)	2470(1)	46(1)
O(11)	12396(2)	3487(2)	2543(2)	56(1)
O(12)	13501(2)	3585(2)	3598(1)	47(1)
O(13)	5151(2)	2775(1)	2227(1)	32(1)
N(1)	5356(3)	989(2)	2655(2)	49(1)
N(2)	5403(3)	2378(2)	4033(2)	49(1)
C(1)	8992(3)	1393(2)	1167(2)	34(1)
C(2)	8989(3)	638(2)	1016(2)	40(1)
C(3)	10141(3)	257(2)	935(2)	45(1)
C(4)	11309(3)	626(2)	1014(2)	41(1)
C(5)	11324(3)	1384(2)	1161(2)	35(1)
C(6)	10167(3)	1766(2)	1231(2)	35(1)
C(7)	7768(3)	1808(2)	1327(2)	37(1)
C(8)	12559(3)	1794(2)	1294(2)	37(1)
C(9)	4371(3)	6369(2)	428(2)	36(1)
C(10)	4148(3)	5638(2)	643(2)	34(1)
C(11)	4423(3)	5421(2)	1364(2)	35(1)
C(12)	4832(4)	5944(2)	1880(2)	46(1)
C(13)	4972(4)	6676(2)	1673(2)	51(1)
C(14)	4782(4)	6885(2)	943(2)	45(1)
C(15)	4223(3)	6594(2)	-368(2)	37(1)
C(16)	4333(3)	4618(2)	1582(2)	39(1)
C(17)	8933(3)	3896(2)	3587(2)	35(1)
C(18)	8925(3)	4033(2)	4343(2)	41(1)
C(19)	10090(3)	4066(2)	4731(2)	45(1)
C(20)	11245(3)	3944(2)	4373(2)	40(1)
C(21)	11260(3)	3801(2)	3614(2)	34(1)
C(22)	10093(3)	3790(2)	3222(2)	34(1)
C(23)	7695(3)	3787(2)	3155(2)	35(1)
C(24)	12480(3)	3616(2)	3219(2)	37(1)
C(25)	4348(5)	651(3)	2934(4)	93(2)
C(26)	4478(6)	92(5)	3442(5)	162(5)
C(27)	5694(7)	-96(5)	3689(5)	141(4)
C(28)	6728(5)	234(3)	3408(3)	72(1)
C(29)	6527(4)	770(3)	2893(3)	63(1)
C(30)	4433(5)	2107(3)	4411(3)	84(2)
C(31)	4625(6)	1644(5)	5000(5)	142(4)
C(32)	5864(6)	1437(4)	5190(4)	112(3)
C(33)	6856(5)	1700(3)	4805(3)	66(1)
C(34)	6593(4)	2187(3)	4244(2)	59(1)

Preparation of $[Zn_4(1,3\text{-}BDC)_3(\mu_4\text{-}O)(pyridine)_2]$ (1). A mixture of $Zn(NO_3)_2\cdot 6H_2O$ (0.207 g, 0.695 mmol), 1,3-$BDCH_2$ (0.115 g, 0.692 mmol), pyridine (6 mL, 2.07 mmol), and H_2O (6 mL) was heated in a 23-mL Teflon-lined autoclave at 150°C for 5 days, and then cooled to room temperature. The yellow crystalline product was filtered, washed with H_2O (2×5 ml) and ethanol (2×5 mL), and air-dried to give crystals of **1** (0.103 g, 0.111 mmol, 63.9% yield). Anal. Calcd for $C_{34}H_{22}N_2O_{13}Zn_4$: C, 44.00; H, 2.39; N, 3.02. Found: C, 44.38; H, 2.95; N, 3.25. IR (KBr, cm^{-1}): 1647, 1609, 1561, 1488, 1450, 1397, 1358, 1218, 1071, 1045, 746, 694 cm^{-1}.

X-ray Structure Determination. All X-ray data were collected with the use of a Siemens P4 diffractometer equipped with a Mo X-ray tube. Intensity data were empirically corrected for absorption with **y**-scan data. All calculations were carried out with the use of SHELXTL programs.[24]

A yellow crystal of **1**, shaped as a block of approximate dimensions 0.48×0.44×0.36 mm, was used for crystal- and intensity-data collection. The unit-cell parameters and systematic absences {*h*0*l* (*h*+*l*=2*n*+1) and 0*k*0 (*k*=2*n*+1)} unambiguously indicated $P2_1/n$ as a space group. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were generated in ideal positions and refined in a riding mode. Details on crystal data and refinement details are given in Table 1. Final atomic coordinates and selected bond lengths and angles for **1** are given in Tables 2 and 3, respectively.

3. Results and Discussion

Preparation. The title compound was prepared by hydro(solvo)thermal reactions. $Zn(NO_3)_2\cdot 6H_2O$ reacts with 1,3-$BDCH_2$ in the presence of pyridine at 150°C for 5 days to give a 1-D zinc coordination polymer with an empirical formula of $[Zn_4(1,3\text{-}BDC)_3(\mu_4\text{-}O)(pyridine)_2]$ (**1**) (eq 1). Yellow crystalline polymer **1** is stable in air and insoluble in common organic solvents. The IR spectrum of **1** exhibits peaks at 1647, 1609, 1561, 1488, 1450, 1397, and 1358 cm^{-1} that can be assigned to the asymmetric and symmetric C=O stretches.[25,26]

$$Zn(NO_3)_2\cdot 6H_2O + 1,3\text{-}BDCH_2 + pyridine \rightarrow [Zn_4(1,3\text{-}BDC)_3(\mu_4\text{-}O)(pyridine)_2] \quad (1)$$

Structure. The monomer unit of polymer **1** with the atom-numbering scheme is shown in Fig. 1. There are four distinct zinc metals in this polymer, each of which is 4-coordinate. The Zn-O bond lengths range from 1.931(2) and to 2.038(3) Å, and the Zn-N bond lengths are 2.062(3) and 2.067(3) Å. The Zn1 and Zn2 are coordinated to four oxygen atoms of 1,3-BDC ligands, and Zn3 and Zn4 are coordinated to three 1,3-BDC oxygens and one pyridine nitrogen. The Zn ··· Zn distances with the range of 3.0445(11)-3.0986(7) Å can be thought of as either very elongated Zn-Zn single bonds or close contacts of those zinc metals. For a compari-

Table 3. Selected bond distances (Å) and bond angles (°) in 1

Zn1-O10	1.957(2)	Zn1-O5#1	1.962(2)	Zn1-O13	1.973(2)
Zn1-O2	2.038(3)	Zn2-O4#2	1.958(2)	Zn2-O7	1.970(2)
Zn2-O13	1.981(2)	Zn2-O11#2	2.030(3)	Zn3-O13	1.935(2)
Zn3-O12#2	1.955(2)	Zn3-O9	1.976(2)	Zn4-O13	1.931(2)
Zn4-O3#2	1.959(2)	Zn3-N2	2.067(3)	Zn4-O1	1.962(2)
Zn4-N1	2.062(3)	Zn3-N2	2.067(3)	Zn1-Zn2	3.0445(11)
Zn2-Zn4	3.0858(7)	Zn1-Zn3	3.0942(8)	Zn2-Zn3	3.0962(8)
Zn1-Zn4	3.0986(7)				
Zn4-O13-Zn3	133.4(1)	Zn4-O13-Zn1	105.1(1)	Zn3-O13-Zn1	104.7(1)
Zn4-O13-Zn2	104.2(1)	Zn3-O13-Zn2	104.5(1)	Zn1-O13-Zn2	100.7(1)

Symmetry transformations used to generate equivalent atoms: #1=$-x+1$, $-y+1$, $-z$; #2=$x-1$, y, z

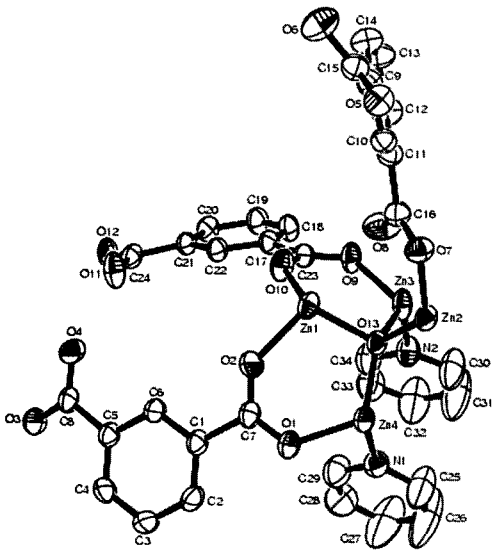


Fig. 1. ORTEP drawing of local coordination of Co with 50% probability thermal ellipsoids.

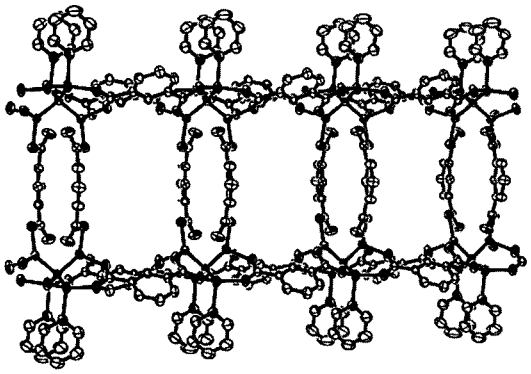


Fig. 2. Packing diagram of polymer 1 on the (011) plane.

son, the covalent radius of zinc is 1.330 Å.

The most striking structural feature of this polymer is the existence of oxygen (O13) bridging four zinc metals. The Zn-O13 bond distances are 1.931(2)-1.981(2) Å, and Zn-O13-Zn bond angles range from 100.7(1) to 133.4(1)°. The bonding parameters around the O13 atom indicate a distorted tetrahedron and a pseudo-sp^3 hybridization of that oxygen atom.

The projection of polymer **1** on the (011) plane demonstrates its one-dimensional structure (Fig. 2). This polymer consists of two strands linked by 1,3-BDC ligands, and each strand is formed by connecting the monomer units by 1,3-DBC ligands.

Acknowledgements

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